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FINAL REPORT

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"CHEMICAL BEAM EPITAXY OF ZnSe"

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INTRODUCTION

ZnSe, ZnTe, and ZnSe/ZnTe layered quantum well structures have room temperature direct energy bandgaps which span the blue/blue-green optical spectrum, thus these II-VI semiconductors possess significant technological potential for visible optoelectronic device applications. Both military and commercial applications are envisioned. Blue/blue-green semiconductor injection lasers for underwater-to-satellite communications, visible flat panel electroluminescent displays, optical disc recording using blue wavelengths to increase the density of recorded information, color laser printers, and short range domestic or industrial communications via polymer fibers are examples of frequently quoted potential markets. The magnitude in U.S. dollars offered by these varied and large commercial markets warrants substantial investment in both research time and funds to push these materials to their ultimate potential for optoelectronic device fabrication, testing, and marketing. Substantial effort is currently underway in Japan and Europe with major investment in funds and manpower.

However, the problems which remain are largely still an issue of availability of suitable materials, specifically availability of p-type ZnSe with sufficient useable hole carrier concentrations. The problem associated with the controlled substitutional incorporation of p-type dopants is currently being addressed by various studies worldwide investigating the growth of ZnSe utilizing the latest advanced nonequilibrium crystal growth technologies. The major amount of effort employs molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD), with new results found in the literature involving chemical beam (CBE) or gas-source molecular beam epitaxy (MOMBE or GSMBE). At the present time all reports involving the growth of wide bandgap II-VI semiconductors by CBE, MOMBE, or GSMBE originate from Japan. One of the motivations of the research program described herein was to establish a chemical beam epitaxy facility in the United States dedicated to the investigation of II-VI materials; at the award date of this contract no such facility existed in the United States. Currently however, the facility at MIT is the only one that the principal investigator is aware of which is dedicated to research on Zn(Se,Te) based semiconductors, although a gas source system is believed to be under assembly at the University of Florida. The funding provided by this Office of Naval Research contract provided essential seed funding necessary to accumulate sufficient funds to build and equip a state-of-the-art chemical beam epitaxy facility at the Massachusetts Institute of Technology. The following final report will describe the facility and its capabilities, and the initial results which have been achieved thus far regarding the chemical beam epitaxy of ZnSe.

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OBJECTIVE

The objective of the program was to determine optimum growth parameters for the chemical beam epitaxy of ZnSe. In addition, microstructural, optical, and electrical characterization of the material was to be performed to assess the material's quality and potential; comparisons were to be made with material grown by molecular beam epitaxy.

CHEMICAL BEAM EPITAXY FACILITY

During the first year of the three year ONR contract, the principal investigator was temporarily located at Purdue University; plans to join the MIT faculty were underway and the initial design of the facility and CBE system were initiated. Once the PI was located on the MIT campus the plans were set in motion. The laboratory which houses the CBE system is presently 100% complete. Figure 1 shows the architectural drawing of the completed laboratory. The remodeling for this project encompassed major renovation of three separate laboratories into one large lab space consisting of a total of 1200 sq ft. (The complete renovation project consisted of remodeling a 2400 sq ft laboratory space which was completely funded by MIT (>\$400K).) As seen in Figure 1, a changing room separates the relatively clean lab from the unclean environment of the corridor of the building. Also included in the laboratory is a substrate preparation facility which consists of two specially designed 8 foot, laminar flow, clean room hoods: one is for solvent use and one is for acid use. The solvent hood was purchased under this contract with funds from the third year allocation. An extensive toxic gas monitoring plan for toxic hydrides has been designed and is currently being implemented to guarantee a safe environment for the project staff, as well as to ensure the safety of the building occupants. Storage of the toxic gases occurs in exhausted toxic gas cabinets with coaxial pipe plumbing of the arsine to the CBE reactor. All hardware containing toxic gas is contained in coaxial enclosures for all locations, with the annular region's exhaust air monitored by separate, redundant toxic gas monitors. Ancillary equipment for the growth experiments includes: (i) an argon ion laser (having both visible and ultraviolet wavelengths) for laser-assisted epitaxy, (ii) a Nomarski interference microscope for investigating surface morphology and surface defects, and (iii) a surface profilometer to measure film thickness.

The chemical beam epitaxy system is modular in design and consists of four separate ultrahigh vacuum (UHV) modules connected to a central UHV transfer module. A schematic drawing of the CBE system is seen in Figure 2. The system consists of an introduction chamber, a substrate preparation chamber, the central transfer chamber, a dedicated II-VI reactor, and an analytical/metallization chamber. All chambers except the analytical/metallization chamber have been delivered and are presently installed in the laboratory. The analytical chamber will be

delivered during the fall of 1990. Depicted in Figure 1 is a second growth chamber dedicated to the epitaxial growth of phosphorus-, arsenic-, and antimony-containing III-V materials. The III-V chamber has been funded through DARPA and is currently in the negotiation stage with commercial vendors.

The substrate preparation chamber (Figure 3) basically consists of a high temperature heating stage for thermal outgassing of sample holders prior to mounting the substrates. Once the substrate is mounted to the substrate holder, the sample with holder is placed onto the introduction chamber (Figure 3) elevator. The elevator can hold up to five 2" wafers. Following roughing of the introduction chamber down to pressures ranging from 10^{-8} to 10^{-9} Torr, the sample is moved from the introduction chamber to the UHV ($\sim 2 \times 10^{-10}$ Torr) transfer chamber (Figure 4). This chamber has around its periphery five "subchamber" ports and five "main" chamber ports which allow for present and future interconnection capabilities. Two "subchambers" which are currently present consist of a storage elevator and another UHV high temperature heating station. The analytical/metalization chamber will be connected to a "main" chamber port and will initially contain an Auger Electron Spectroscopy (AES) system. However the chamber has been designed to provide significant future flexibility by containing ports for: electron beam guns for metal evaporation, reflection high energy electron diffraction (RHEED) with associated phosphor screen, two laser ports, and argon ion sputtering. The new analytical/metalization chamber will allow *in situ* metalization studies, as well as analysis by AES of surfaces which have been irradiated with a coherent photon beam. These particular studies will be invaluable for understanding possible outcomes of the laser-assisted growth experiments.

Figure 5 is a photograph of the II-VI-dedicated growth reactor. The II-VI reactor is a molecular beam epitaxy (MBE) system which has been configured to utilize gaseous chemicals for the source materials, such as various metalorganic compounds and hydrides. The gases are inserted into the reactor via four high temperature gas injectors which can thermally decompose the compounds if sufficiently high temperatures are used. Thus flux ratios of the sources are accurately controlled by precision mass flow controllers. The system is also equipped with three effusion cells as is typically employed in MBE when solid sources are required. The gases which currently exist on the system are diethylzinc, diethylselenide, trimethylindium, triethylgallium, and arsine. The hardware necessary to add diethyltelluride, hydrogen selenide, dimethylzinc, and ammonia is being acquired to be placed in the space provided in the gas manifold. *In situ* analysis capabilities include RHEED to monitor qualitatively the microstructure and surface reconstruction, a quartz crystal monitor to measure absolute flux rates of the solid sources, and ports available for (i) optical pyrometers to consistently calibrate the substrate temperature, and (ii) laser ports to illuminate the substrate surface with coherent radiation parallel to the surface and perpendicular to the surface. The pumping system of the growth chamber consists of a 400 l/s ion pump, a 3500

1/s cryopump, and a 2300 1/s diffusion pump which provides a 10^{-11} Torr base vacuum.

ACHIEVEMENTS

Thus far we have grown by metalorganic molecular beam epitaxy two ZnSe epitaxial layers onto (001)GaAs substrates. The substrate was organically cleaned and etched in a 5 H₂SO₄:1 H₂O₂:1 H₂O solution at 60°C for 80 seconds to remove 10 μ m of the mechanically polished and damaged surface. During the rinsing of the substrate a GaAs oxide is grown to passivate the surface during mounting and transfer of the sample to the introduction chamber. The metalorganic source gases were diethylzinc (DEZn) and diethylselenide (DESe) each having flow rates of 1 sccm; both gases were thermally decomposed by injecting the gases into the UHV chamber through high temperature "cracking" zones. During the growth the DEZn was cracked at 350°C, whereas the DESe was cracked at 850°C. The growth temperature was maintained at 325°C, following calibration using the eutectic phase change of 500Å Au on Ge (356°C) and the oxide desorption temperature of the GaAs oxide (580°C). The film thicknesses were 500Å and 1200Å. Figure 6 shows the reflection high energy electron diffraction patterns obtained following the growth of the thin 500Å ZnSe layer. The 500Å ZnSe film was the first material grown with the new CBE system and the first ZnSe grown by the metalorganic molecular beam epitaxy technique in the United States. Figure 6(a) shows the [110] azimuthal direction of the (001)-oriented single crystalline ZnSe film, whereas Figure 6(b) shows the [010] azimuthal direction. The two-fold reconstruction which is present in the [010] azimuth indicates that the surface is Zn-stabilized. This observation is consistent with the growth parameters which were used as the DEZn flow rate was 1 sccm and the DESe flow rate was 0.32 sccm. Investigating the surface morphology with Nomarski interference microscopy indicated a featureless surface at 1000X magnification. Due to the thinness of the films, optical and electronic characterization has not been performed thus far.

PRESENT STATUS

At the present time the CBE system is undergoing a modification of the transfer arm which transfers the sample from one UHV chamber to another. Once the new design is implemented, the growth experiments will continue. The main issue to be addressed immediately is the very low growth rate. The low growth rate may be due to a low growth temperature and/or a low flow rate. Both parameters and their affect on the growth rate will be assessed in the beginning growth experiments. Once the growth rate is increased to that typically employed ($\sim 1 \mu\text{m/hr}$), films which are moderately thick ($\sim 3\text{-}4 \mu\text{m}$) will be analyzed for their material properties including optical, electronic, and microstructural characterization.

PUBLICATIONS

a. Papers Submitted to Refereed Journals (and not yet published)

- none

b. Papers Published in Refereed Journals

- R. L. Gunshor and L. A. Kolodziejski, "Recent Advances in the Molecular Beam Epitaxy of ZnSe and its Superlattices (INVITED)," *IEEE Trans. on Quantum Electronics, Special Issue on Quantum Well Heterostructures and Superlattices* vol. QE-24(8), pp. 1744-1757, 1988. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)
- Q. D. Qian, J. Qiu, M. R. Melloch, J. A. Cooper, Jr., R. L. Gunshor, and L. A. Kolodziejski, "Electrical Characterization of the Epitaxial ZnSe/ Epitaxial GaAs Interface," *Applied Physics Letters*, vol. 54(14), pp. 1359-1361, 1989. (Supported by Office of Naval Research, Defense Advanced Research Projects Agency)
- M. Vaziri, R. L. Gunshor, L. A. Kolodziejski, S. Venkatesan, R. F. Pierret, and R. Reifengerger, "Optical and Electrical Characterization of ZnSe Doped with Gallium," *Journal of Vacuum Science and Technology*, vol. B7, pp. 253, 1989. (Supported by Office of Naval Research, Defense Advanced Research Projects Agency, and Air Force Office of Scientific Research)
- S. Venkatesan, R. F. Pierret, J. Qiu, M. Kobayashi, R. L. Gunshor, and L. A. Kolodziejski, "Deep Levels in Ga-Doped ZnSe Grown by Molecular Beam Epitaxy," *Journal of Applied Physics*, Vol. 66(8), pp. 3656, 1989. (Supported by Office of Naval Research and Defense Advanced Research Projects Agency)
- Q. -D. Qian, J. Qiu, M. Kobayashi, R. L. Gunshor, L. A. Kolodziejski, M. R. Melloch, J. A. Cooper, J. M. Gonsalves, and N. Otsuka, "Low Interface State Density at Pseudomorphic ZnSe/Epitaxial GaAs Interface," *Materials Research Society Symposium*, Vol. 45, pp. 423-428, 1989. (Supported by Office of Naval Research and Defense Advanced Research Projects Agency)

c. Books (and sections thereof) in Publication

- R. L. Gunshor, L. A. Kolodziejski, M. R. Melloch, N. Otsuka, and A. V. Nurmikko, "II-VI/III-V Heterointerfaces: Epilayer-on-Epilayer Structures" in Growth and Optical Properties of Wide-Gap II-VI Low Dimensional Structures, T. C. McGill, C. M. Sotomayor Torres, and W. Gebhardt, Eds., Plenum Press: New York, 1989, pp. 229-238. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)
- L. A. Kolodziejski, R. L. Gunshor, A. V. Nurmikko, and N. Otsuka, "Exciton Self-Trapping in ZnSe/ZnTe Superlattice Structures" in Growth and Optical Properties of Wide-Gap II-VI Low Dimensional Structures, T. C. McGill, C. M. Sotomayor Torres, and W. Gebhardt, Eds., Plenum Press: New York, 1989, pp. 269-279. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)
- L. A. Kolodziejski, R. L. Gunshor, and A. V. Nurmikko, "II-VI Compound Strained-Layer Superlattices," in Strained Layer Superlattices, R. B. Biefeld, Ed., Switzerland: Trans Tech Publications, 1989, Vol. 21, pp. 199-230, 1989. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)
- R. L. Gunshor, L. A. Kolodziejski, A. V. Nurmikko, and N. Otsuka, "Molecular Beam Epitaxy of II-VI Semiconductor Microstructures," in Semiconductors and Semi Metals, R. Pearsall, Ed., Boston: Academic Press, 1989, galley stage. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)
- L. A. Kolodziejski, R. L. Gunshor, A. V. Nurmikko, and N. Otsuka, "Molecular Beam Epitaxy of Wide Gap II-VI Semiconductor Heterostructures," in Molecular Beam Epitaxy, R. F. C. Farrow and J. R. Arthur, Eds., New York: Noyes Publishers, 1990, submitted. (Supported by Office of Naval Research, Air Force Office of Scientific Research, Defense Advanced Research Projects Agency, and National Science Foundation)

d. Invited Presentations at Topical or Scientific/Technical Society Conferences

- R. L. Gunshor, L. A. Kolodziejski, and A. V. Nurmikko, "ZnSe/MnSe Magnetic Semiconductor Superlattice," presented at the *Warren E. Henry Symposia on Magnetism*, Washington, D. C., August 1988.
- A. V. Nurmikko, R. L. Gunshor, and L. A. Kolodziejski, "Optical Characterization of Wide Bandgap II-VI Multiple Quantum Wells," presented at the *5th International Conference on Molecular Beam Epitaxy*, Sapporo, Japan, August, 1988.
- R. L. Gunshor, L. A. Kolodziejski, N. Otsuka, and A. V. Nurmikko, "II-VI/III-V Heterostructures," presented at the *Meeting of the Electrochemical Society*, Chicago, October, 1988.
- R. L. Gunshor, L. A. Kolodziejski, N. Otsuka, A. V. Nurmikko, and M. Kobayashi, "II-VI/III-V Heterostructures," presented at the *SPIE Conference on Monitoring and Control of Plasma-Enhanced Semiconductors*, Santa Clara, November, 1988.
- A. V. Nurmikko, R. L. Gunshor, and L. A. Kolodziejski, "Excitons and Phonons in Widegap II-VI Compound Semiconductor Superlattices," presented at the *SPIE Symposium on Lasers and Optics*, Los Angeles, 1989.
- R. L. Gunshor, L. A. Kolodziejski, M. Kobayashi, A. V. Nurmikko, and N. Otsuka, "Wide Gap II-VI DMS Superlattices: MBE Growth and Characterization," presented at the *Spring Meeting of the Materials Research Society*, San Diego, 1989.
- R. L. Gunshor, M. Kobayashi, L. A. Kolodziejski, and A. V. Nurmikko, "Wide Gap II-VI Heterostructures," presented at the *International Conference on II-VI Semiconductors*, Berlin, 1989.
- R. L. Gunshor, M. Kobayashi, L. A. Kolodziejski, A. V. Nurmikko, and N. Otsuka, "MBE of Wide Bandgap II-VI Compounds," presented at the *International Conference on Crystal Growth*, Sendai, Japan, 1989.

- L. A. Kolodziejski, "Modern Growth Technologies of Semimagnetic Semiconductors," presented at the *International School on Physics of Semiconducting Compounds*, in Jaszowiec, Poland, April, 1990.
- L. A. Kolodziejski, "Semimagnetic Semiconductor Superlattices: MBE Growth and Characterization," presented at the *European Materials Research Society Meeting* in Strasbourg, France, May, 1990.
- L. A. Kolodziejski, "Chemical Beam Epitaxy for Advanced Optoelectronic Devices," to be presented to the *Optical Society of America*, Boston, November, 1990.

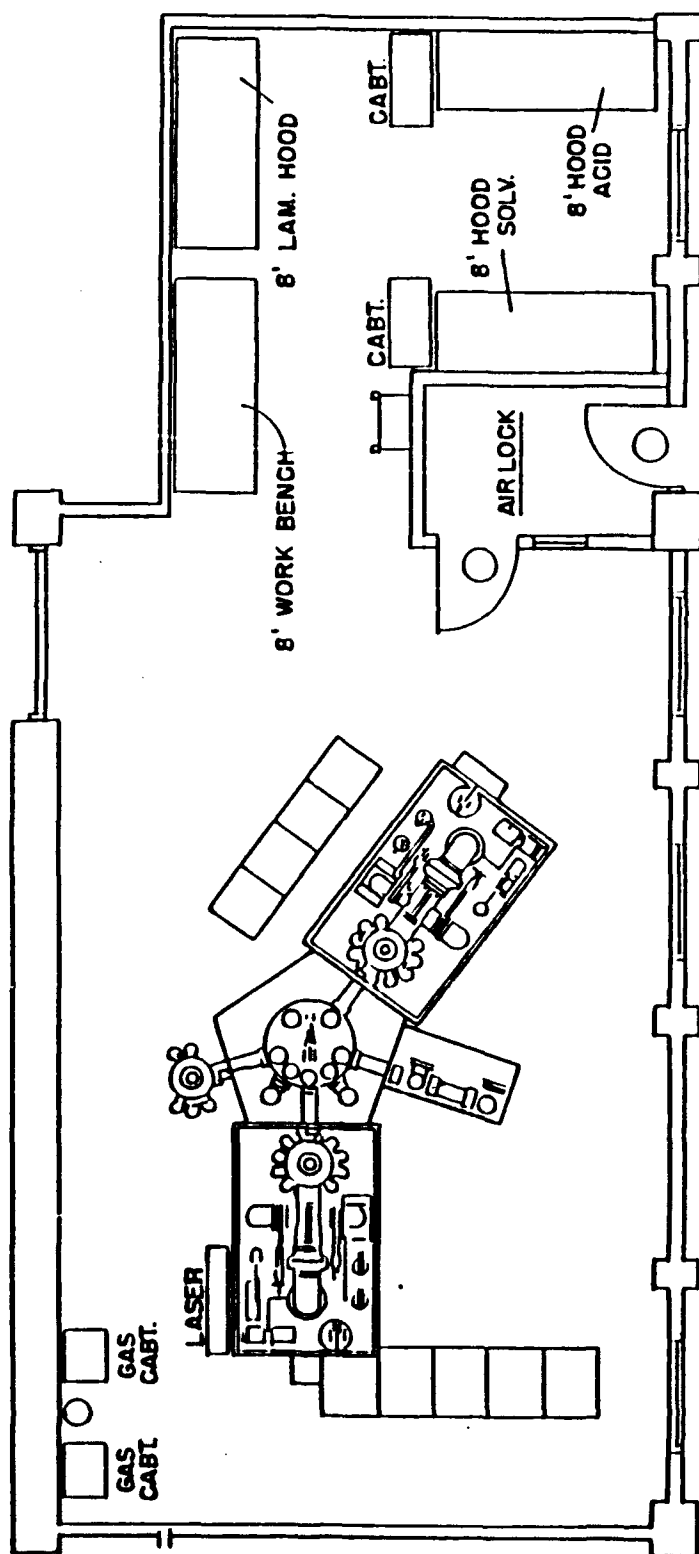


Figure 1: Architectural drawing of the 1200 sq. ft. chemical beam epitaxy facility. The main features of the lab are label in the figure.

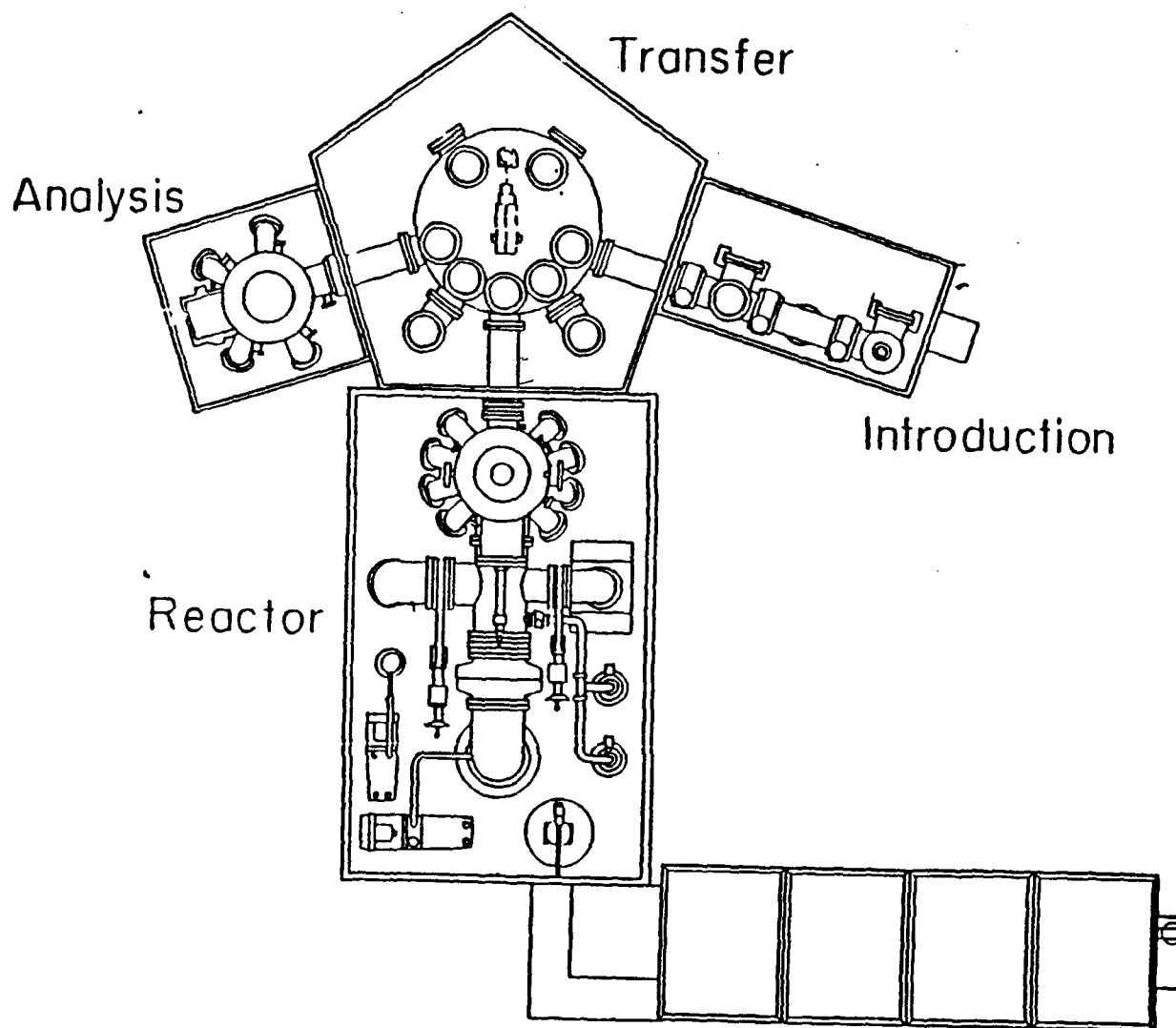


Figure 2: Schematic drawing of the layout of the chemical beam epitaxy system. The growth chamber, analytical/metalization chamber, transfer module, and introduction chamber are shown with considerable detail. The approximate dimensions are 17 ft. x 25 ft.

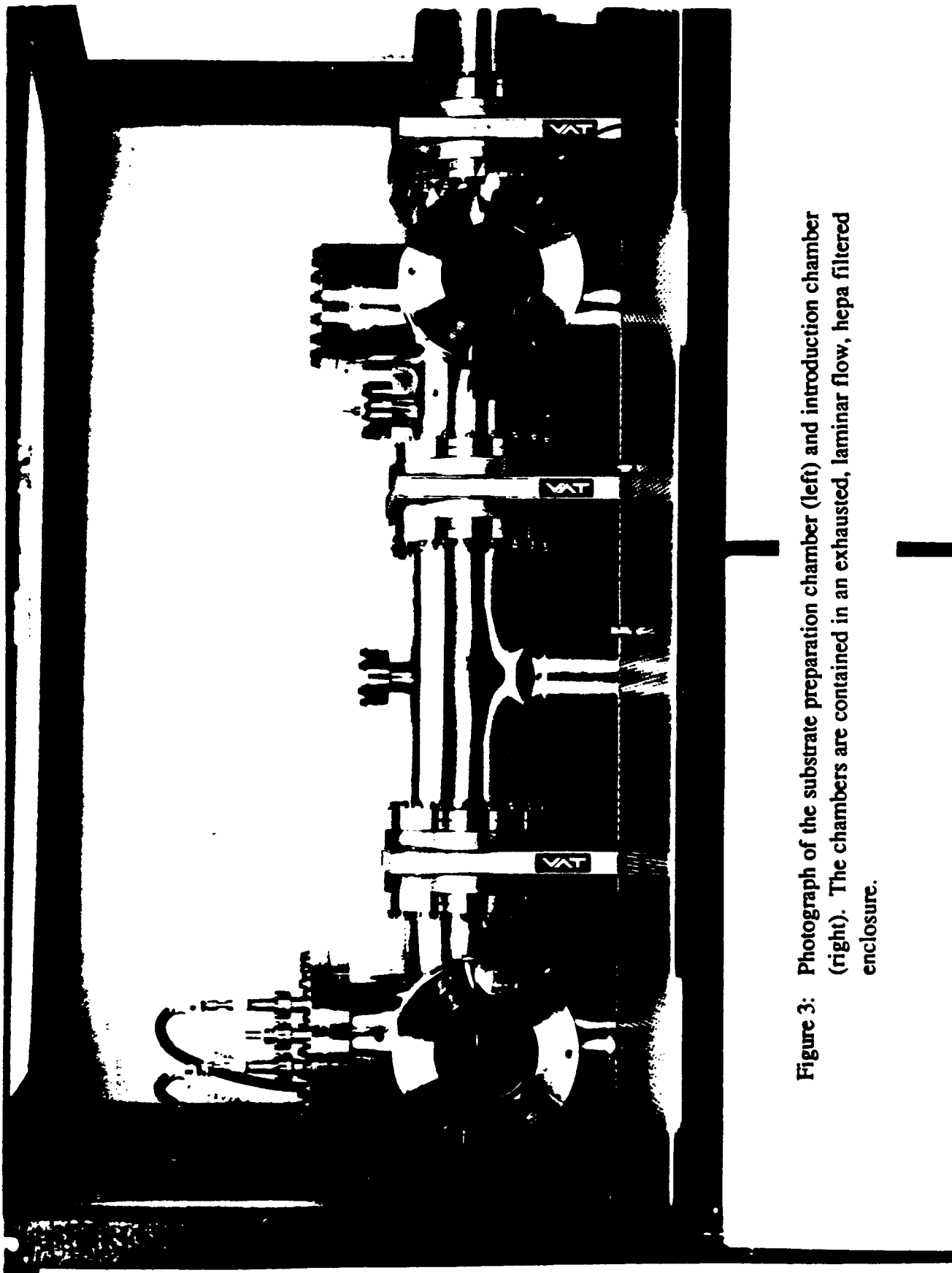


Figure 3: Photograph of the substrate preparation chamber (left) and introduction chamber (right). The chambers are contained in an exhausted, laminar flow, hepa filtered enclosure.

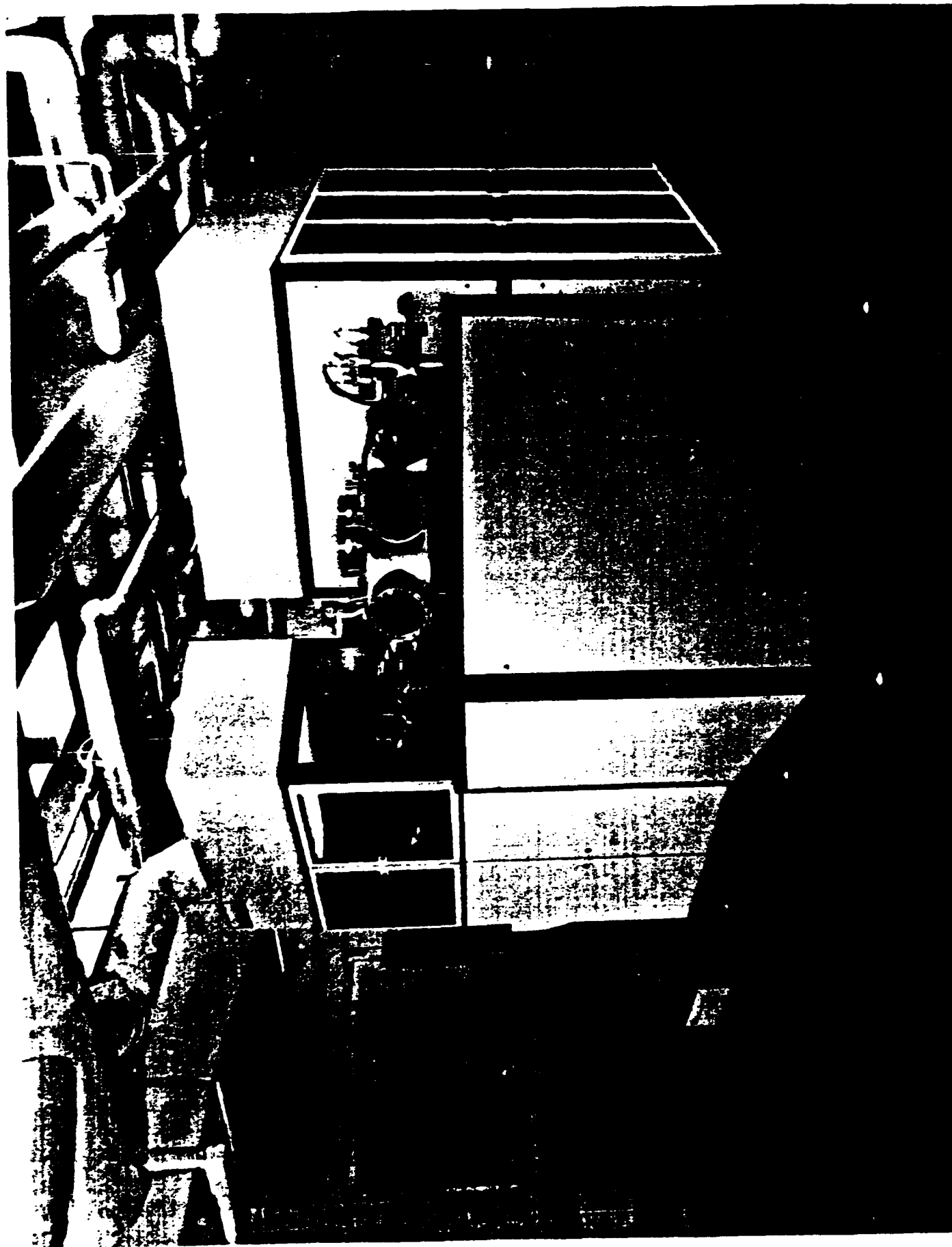


Figure 4: Photograph of the UHV transfer module. Interconnecting chambers are attached around its periphery with samples transferred via a rotating transfer arm or "fork".

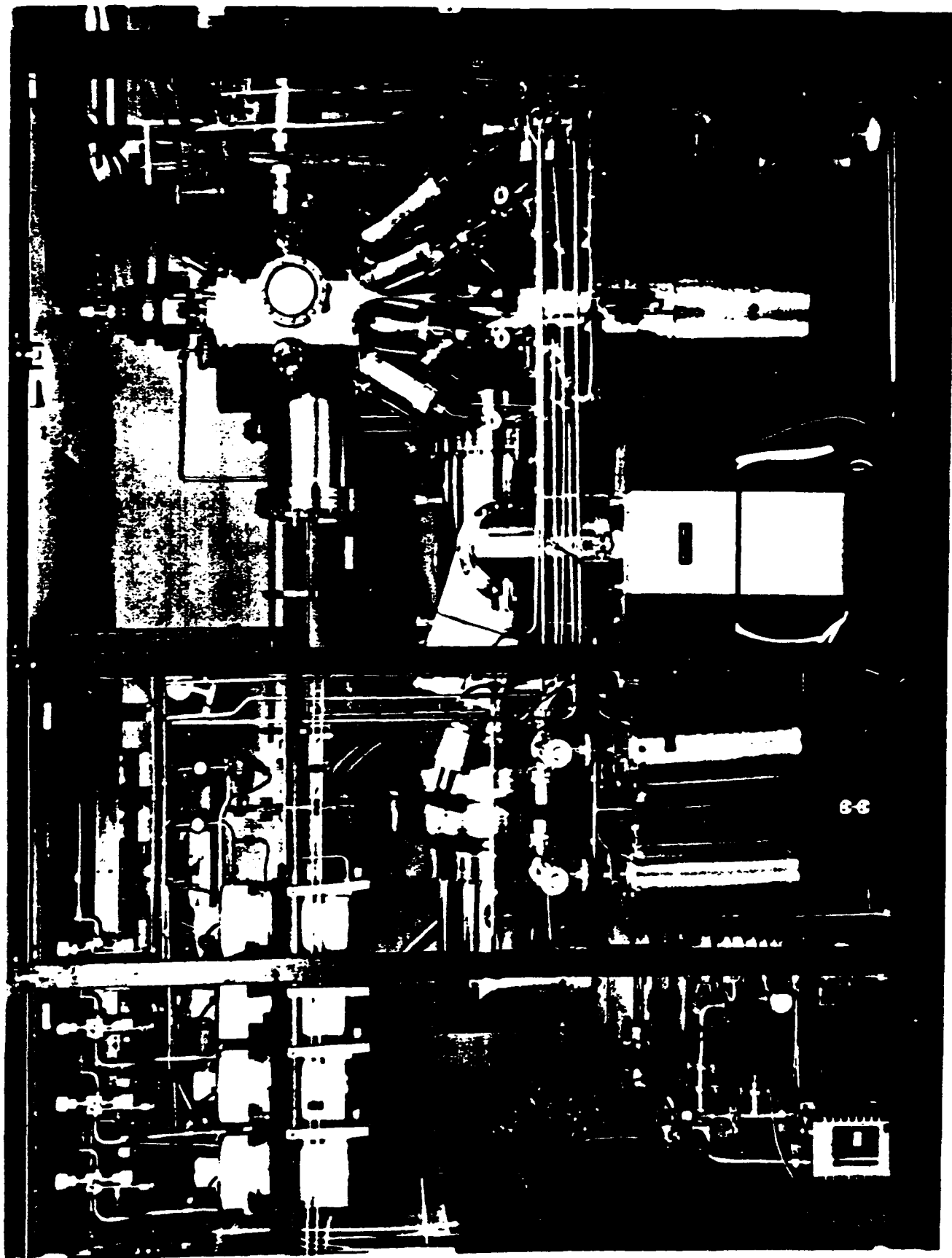


Figure 5: Photograph of the II-VI-dedicated growth reactor. The growth chamber is shown with the associated pumping subsystem (bottom left) and the attached gas manifold (top left). The entire system is enclosed in an exhausted, laminar flow, hepa filtered enclosure for added safety and cleanliness.

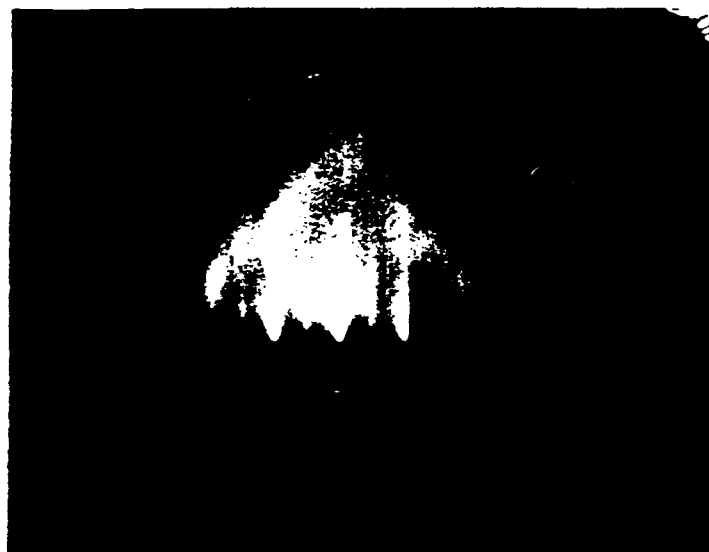


Figure 6: Reflection high energy electron diffraction patterns obtained following the growth of the 500Å ZnSe film. (a) represents the pattern observed in the [110] azimuth and (b) represents the pattern observed in the [010] azimuth. The two-fold reconstruction indicates a Zn-stabilized surface.

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